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STUDY DIRECTED TOWARD SELECTION OF APPARATUS
FOR ANALYSIS OF LUNAR CRUST AND ATMOSPHERE

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INTRODUCTION

This study is directed toward the instrumentation problems associated with the analysis of the lunar crust and atmosphere by mass spectrometry. Based on a survey of the present knowledge and theories of the lunar characteristics, a major portion of this study is concerned with the type of mass analyzer which holds the greatest potentialities for this specific application.

The lunar environment has been considered with emphasis being given to its influence on the instrumentation package.

The characteristics of the various types of ionic mass analyzers have been reviewed and their potentialities for use in the lunar environment are discussed.

Since it is obvious that presently-available instrumentation is quite unsuited for use on a lunar mission, consideration is given to the areas of knowledge which need to be supplemented. After this additional information has been assembled, the design of instrumentation for this application can be done more intelligently.

It is highly desirable that the state-of-the-art in the field of mass spectrometry be greatly improved before the design of flyable apparatus is started. There are many facets of this problem which need serious attention and study. This report mentions some of them and suggests experiments which can be devised to shed important light on these factors.

LUNAR ENVIRONMENT

Much is known about the lunar environment, but there is much uncertainty about some of the important parameters. For instance, the temperature range is well established as varying between 400°K at mid-day to 120°K at night time, but the pressure and composition of the atmosphere are merely estimated.

Estimates of the pressure indicate that it is much too low for the lunar atmosphere to protect the surface of the moon from solar radiation. This radiation includes photons of a very wide energy range as well as charged particles, sometimes called solar wind. The presence of the high photon flux makes the detection of minute ion currents more difficult. The ion current sensor electrodes must be well shielded from this photon flux, to prevent the masking of ion currents by currents due to secondary electrons which are released by the photons.

If the pressure and density of the gas on the moon is as low as best estimates indicate, the mean free path of molecules leaving the moon will usually be that of the trajectory until they strike the moon again. Thus, when sampling the atmosphere of the moon, it may be quite important to admit to the ionizing region of the mass spectrometer only those molecules which are approaching the surface. These are molecules which left the moon at some remote point and therefore are likely to be little influenced by any contaminating effect of the vehicle and its retrorockets.

INFLUENCE OF ENVIRONMENT ON THE MASS SPECTROMETER

The mass spectrometer system which is sent to the moon must be capable of operating within the above-mentioned wide temperature range. This presents thermal control problems. Many electronic circuits will be composed of solid state devices. These solid state components have a prescribed operating temperature range which will most certainly be narrow relative to the ambient temperatures on the moon. It seems certain that heat sources will be required to prevent the temperature falling to limits which are too low at night time. It is possible that precautions will need to be taken to limit the high temperature during operation in the day time.

For satisfactory operation during the lunar day, the instrumentation package must be designed with the photon and particle flux from the sun being kept in mind. The ion current sensing electrodes must be protected from all photons. These include not only those which originate at the sun, but those which result from the impingement of the charged particles upon the environs of the apparatus.

The volume from which the ions are collected must be essentially nude; it must project from the mass analyzer package in such a manner that the molecules of the crust, when volatilized, can be made to pass through this region. When the analyzer is being used to sample the lunar atmosphere, consideration must be given to the direction from which the

incident molecules are accepted into the ionizing region.

Because of the lowered velocity of escape for molecules on the moon relative to that on the earth, it is anticipated that the concentration of the lighter elements in the lunar atmosphere will be very low. In fact, the density of molecules of mass below 40 is through to be quite low. On the other hand, the surface of the moon is constantly under bombardment by protons from the sun. Not all of these protons escape immediately, thus the contribution of hydrogen to the lunar atmosphere should be finite and not zero. Hydrogen, in the form of water which is bound to the rocks may also be present on the moon. Similarly, helium is constantly being supplied to the lunar atmosphere from the decomposition of radioactive material. Further, it is assumed that the lunar crust may contain elements which extend to the top of the periodic table. Thus it seems that the mass range should extend through all of the known elements of the periodic table.

The sensitivity and the dynamic range of the mass spectrometer system should both be as large as is feasible. Only when this is done can the analyses of the less abundant components of the crust and the atmosphere be made.

CONSIDERATION OF MASS ANALYZER TYPES

Of the many types of mass spectrometers which have been used or proposed which type holds the highest potential of meeting the requirements and the demands of operation on the moon? In the search for an answer to this question, it seems most reasonable to eliminate at once all types of mass spectrometers which have not been able to compete effectively with the other types for laboratory use, regardless of other attributes. This consideration eliminates the Farvitron and the Bennett types of mass spectrometers. This is true even though these mass spectrometers are non-magnetic, light in mass and have other merits.

Because of the requirements for other instrumentation which is to accompany this payload, it has been stated that the stray magnetic field from the mass spectrometer package must be limited to the order of one gamma or ten microgauss. This consideration eliminates many of the mass spectrometers which are frequently used in the laboratory. To be specific, this eliminates all types of magnetic sector instruments, cycloidal instruments, and omegatrons.

Thus far, all known types of mass spectrometers which were available during World War II have been eliminated.

Fortunately, since World War II several types of non-magnetic mass spectrometers have been proposed. Of these, two have found use in laboratories, and on space vehicles.

Taking advantage of the war-time development of radar with its refined timing techniques, W. E. Stephens⁽¹⁾ in 1946 proposed a velocity-type mass spectrometer. A group of ions which are formed during a very small time interval are all given the same energy and directed toward a drift tube. The velocities of the ions in the drift tube are mass-dependant and therefore their transit times are mass-dependant. Through the observation of the transit times of the ions, information about their mass-to-charge ratio is obtained. Although this mass analyzer is really a velocity-sensitive device, it has been called the non-magnetic time-of-flight mass analyzer. The term "non-magnetic" is used to differentiate it from an earlier instrument proposed by Goudsmit in which the particles move on circular orbits in a magnetic field.

In 1953, Paul and Reinhard⁽²⁾ published an article in which they called attention to the possibilities of making a mass spectrometer whose operation is based upon the solutions of the Mathieu equation. In 1958, Paul, Reinhard and von Zahn⁽³⁾ published a rather lengthy article in which they discussed further the application of the Mathieu equation to the operation of the quadrupole mass filter. In this article, they also show interesting experimental results. In 1963, von Zahn⁽⁴⁾ published results of experiments using a single rod in an instrument which he called the "monopole". The fields in the monopole are identical to the fields in one 90° sector of the quadrupole and hence the motions of the ions are also identical. Because the monopole has no particular advantage

over the quadrupole and it does have serious disadvantages, it is not considered as a mass analyzer for the lunar explorations.

TIME-OF-FLIGHT MASS ANALYZER

As has been mentioned, the first description of the linear time-of-flight was by Stephens. However, Berry and Koppius proposed the same idea at about the same time. Further, Glenn and Bay also have suggested variations of the original time-of-flight instrument.

The first commercially-available time-of-flight instrument was produced by Bendix in 1955.⁽⁵⁾ Although the time-of-flight instrument has not been a serious competitor of the more conventional magnetic instruments for use in the laboratory, it has found acceptance for specialized applications. These specialized applications include the following of phenomena which vary rapidly with time, such as reaction studies, flame studies, etc. It is particularly suited to these applications because it makes 10,000 analyses each second. The fact that a complete spectrum is displayed during each analysis can sometimes be used to partially offset the disadvantage of the low duty cycle on the operation of the source. In the laboratory, this information can be transmitted and stored. On the moon, the telemetry channels will be of much too narrow bandwidth for the transmittal of the information at this rate. For this application, it is necessary therefore, to scan the masses one at a time at a slow rate. Thus, the additional information which accrues from the fact that the entire spectrum is displayed 10,000 times per second is lost so far as the information on the masses other than the

one being observed is concerned.

The time-of-flight instrument has a number of characteristics which limit its applicability for lunar exploration.

The successful operation of the time-of-flight instrument requires that the ions be formed in a sheet of minimal thickness in a very short period of time. The thickness of the ionization sheet is in the order of a few millimeters and the duration of the ionization pulse is the order of a quarter microsecond. The Bendix time-of-flight instrument uses a magnetic field to collimate the ionizing electron beam. Without the assistance of a magnetic field, it is most difficult to contain the electrons in a thin sheet. In the presence of a magnetic field, a moving ion is given a transverse acceleration. The impulse given to the ion as it moves through the magnetic field in the source region is neutralized or offset by an equal and opposite impulse as it passes through a second magnetic field of the opposite polarity.

The Bendix time-of-flight instrument uses a magnetic secondary emission multiplier. The magnetic field leads to a multiplier of the required high speed, but more importantly, it presents a planar target to the ion beam. The incremental difference in the flight time of adjacent masses is quite small. It is essential that the trajectory lengths of all ions be similar. Otherwise, the difference in the transit times of the different paths becomes too large a fraction of the time difference between ions of adjacent masses.

Because the time-of-flight instrument is a "batch" device, the ionizing electron beam is turned on intermittently and is on only about 1% of the time. This is a most severe limitation of the total number of ions to which the instrument can respond in a given length of time. Space charge conditions in the ion source preclude the use of an ionizing beam which is more intense during the short time than what can be used under steady-state conditions. Therefore, the low duty cycle must result in a proportionately decreased transport of ions. This is a most serious disadvantage under conditions which demand the ultimate in sensitivity. Further, the ions which enter the drift space must be moving in directions which are very nearly parallel. Small components of transverse velocity cause the ions to miss the target at the end of the drift space.

The analytical accuracy of the time-of-flight instrument is low. The small number of ions in a given analysis or batch, causes a very large fluctuation of the number of ions in successive batches. This comes about purely from the laws of statistical fluctuations. Components present in low concentration appear only occasionally; most batches contain no ions of these species.

QUADRUPOLE MASS FILTER

The quadrupole mass filter is almost unique among mass spectrometer types in that it operates entirely satisfactorily without the aid of any dc magnetic fields. This feature completely eliminates the requirement for magnetic shielding on the lunar experiment. The quadrupole transmits ions on a continuous basis. That is, the duty is 100%. Further, the mass analyzer is completely indifferent to the time and place of ion formation. Relative to other mass analyzers, the quadrupole exhibits large tolerance to the direction and velocity of the incident ions.

The quadrupole mass filter is unusually flexible. That is, its mode of operation is readily variable. In particular, it is a very simple matter to increase the sensitivity by lowering the resolution. For use on the moon, it is proposed that the resolution-sensitivity adjustment be varied in a prescribed manner. This will permit the observations of low intensity peaks which are isolated from more dominant peaks at the maximum sensitivity. Further, it will permit the resolution of dominant peaks even though they are close together on the periodic table. The ultimate in sensitivity is obtained by operation in the high-pass filter mode. Under these conditions all ions heavier than an arbitrarily set value are transmitted through the instrument.

The quadrupole mass filter is less than 10 years old. It is becoming popular and is finding wider use in the laboratory during the past

several years. Refinements in the structure and in the modes of operation of the instrument have come slowly. This is due in no small part to the complexity of the theory of its operation. The formal theory which describes the ionic trajectories is given by the solutions of the Mathieu equation. Unfortunately, the trajectories depend in a very important manner upon a great number of independent variables. These include the voltage and frequency of excitation, the ratio of the dc to the ac potentials, the mass-to-charge ratio of the ion, the phase of the ac excitation when the ion enters the quadrupole, and the position, angle, and velocity with which the ion enters the entrance aperture.

When the momentum impulse which the ion receives as it passes through the fringing field is ignored, the solutions of the Mathieu equation permit the calculation of the trajectory. However, the equations of motion are given in infinite series, the coefficients of which are continued fractions. There are no simple first-order solutions, even to the equations of the trajectories.

The correlation of the operating characteristics such as resolution, ion transport efficiency, with the many independent parameters of ion energy, aperture geometry, voltage and frequency of excitation is most difficult and cumbersome through the use of the Mathieu equation. This situation has been and is responsible for the slow rate of progress in the refinement of the quadrupole mass filter.

We have by-passed the Mathieu equation and have used a more direct

approach to the equations of the envelopes which contain the trajectories.⁽⁶⁾ Considerable progress has been made in correlating the performance of the quadrupole with the operating parameters of ion energy, voltage and frequency of excitation, entrance geometry, etc. These equations have been most helpful in the interpretation of our experiments. In the refinement of the quadrupole mass filter for use on the moon, it is obvious that these same equations would be most helpful both as to guide our experiments and to aid in the interpretation of the results.

Based on the performance data which we have from the use of the quadrupole mass filter, it has demonstrated high capability for uses of this kind. Further experimentation directed toward increasing the mass range to higher values, and the development of a high sensitivity ion source would lead to the design of a mass analyzing system quite superior to any which is presently available.

STATE-OF-THE-ART IMPROVEMENTS DESIRED

1. General

No available solids analytical mass spectrometer is suitable for transportation to the moon and operation by remote control. The high performance solids analytical mass spectrometers of the Mattauch-Herzog type are much too large, too heavy and they use magnetic fields. Further, the ion sources used with these instruments are usually of a spark type which is combined with the photographic plate for time integration of the resolved peaks.

The instrument which we believe offers the greatest possibility of success in this project is the quadrupole mass spectrometer. However, further developments and refinements as outlined and discussed below are required to optimize a suitable system for this program.

a. Sample Vaporization

New ion source developments are needed. If the masses are to be scanned one at a time, the ion yield from the source should be constant both in magnitude and in composition as a function of time. No such sources are available commercially today.

The most pressing state-of-the-art improvements are concerned with the ion source. Foremost of these problems is the sample vaporizing means. The problem under consideration here does not include the physical one of transporting the lunar crust to the vicinity of the mass spectrometer.

The problem under consideration here involves simply the vaporization of the sample so that it can be introduced to an ion source.

By what means can the solids of the lunar crust be vaporized and subsequently ionized for mass analysis? Vaporization usually results from the heating of the sample to very high temperatures. How can the material of the lunar crust be heated to a very high temperature? Since we must assume that it cannot be made a part of an electrical circuit for resistance heating, it must be heated by the impingement of energetic particles onto its surface.

What projectiles are available for impingement on the lunar crust material? One thinks immediately of photons, electrons or heavier charged particles. The latter may be protons, alpha particles or charged nuclei of a heavier element.

Heating by all of these particles has been observed in the laboratory. Heating by photons is done either by solar furnaces or by lasers. Electron beams are being used for metal cutting and welding applications. The phenomenon of cathode erosion by charged particle bombardment has been known for many decades. It is commonly called sputtering. This process accounts for the darkening of the glass tubes in glow discharges.

The choice of the bombarding particle and the techniques for their use will be greatly influenced by the manner in which the material of the lunar crust is presented to the vaporizer. That is, it makes a difference whether the material is presented to the mass spectrometer

system as a powder which is introduced at a slow but steady rate or whether it is presented as a chunk of solid material from which the sampling is to be made.

If the lunar crust is presented as a fine powder the possibility exists of volatilizing it by applying it at a slow but steady rate to a very hot surface. This hot surface could be a tungsten or tantalum ribbon filament heated to a very high temperature.

It is desired that the sizeable chunk of material be vaporized in such a manner that the average temperature of the assembly is raised only modestly. If the entire sample is heated to a high temperature the more volatile materials evolve first, the less volatile later. Under these conditions integration of the peaks with time is required for an analysis. Vaporization at low average sample temperature is accomplished by either of two means: first, if the bombardment is by heavy charged particles, each of which will raise the local temperature in a micro volume to a very high level, that would achieve our goal. If, on the other hand photons or electrons are used, other techniques must be adapted. Since each individual photon carries only a small amount of energy, a very great flux density of photons is required in order to raise the temperature to a high level. This can be accomplished by the focused beam from a laser. A pulsed laser which gives a very short burst of very high energy is most suitable for this application.

Electrons individually may be as energetic as ions which have been

accelerated through applied potential differences. However the electron does not lose all of its energy in a very short distance in a solid material as does the heavier particle. Therefore, if electron beam heating is applied, techniques similar to those of lasers must be used. That is, the electron flux must be very great and for very short periods of time to minimize large overall heating.

More detailed discussions of each of these proposed means of volatilization of the crust are contained in later sections of this report.

b. High Efficiency Ion Source

As mentioned earlier in this report, the quadrupole mass spectrometer is very tolerant to the place and time of the ion formation. As a mass analyzer the quadrupole is so new that to the author's knowledge no ion source has been developed which fully exploits this characteristic.

If the means used to volatilize the lunar crust does not simultaneously ionize a sufficient portion of the molecules, ionization must be accomplished by another device. The device proposed for this ionization is an electron bombardment ion source. By giving careful consideration to the influences of space charge and to the separation of heavy positive ions from the low mass ionizing electrons, it should be possible to design a very efficient ion source for use with the quadrupole. This ion source should be at least an order of magnitude more sensitive than the usual mass spectrometer ion source.

2. Mass Analyzers

The mass analyzer which we consider to hold the greatest promise for operating on the moon is the quadrupole mass filter. It has demonstrated its capabilities for use on rocket-launched vehicles, for the exploration of the composition of the earth's atmosphere. Further, it is finding its way into many laboratories. Its potentialities have been only partially explored. In particular, more information is needed about its operation at the higher masses.

Experiments in which mass analyses are made at mass 200 or higher should be conducted with quadrupoles of different sizes. Experimental data which correlate the transmission efficiency and resolution of quadrupoles of different sizes are needed in order to design a quadrupole of optimum dimensions to perform the required analyses.

a. Integration of Ion Source and Quadrupole

It has been suggested that a super-sensitive ion source be developed, and that the dimensions of the quadrupole be chosen to give the required resolution and sensitivity. When these two tasks are accomplished, the two pieces of equipment can be integrated into a single unit. The overall performance of the system is somewhat dependant upon the manner in which the ions are injected into the quadrupole. Higher transmission efficiencies are obtained when the ions are introduced into the quadrupole through a small aperture, and in a direction parallel to the instrument axis.

A series of experiments is required to determine the most appropriate geometry of the electrodes at the entrance to the quadrupole.

3. Quadrupole Support Structure

A study should be made of the various manners in which four cylindrical surfaces can be appropriately positioned for this application. As the resolving power is extended to higher values the tolerances on the physical dimensions of the assembly become smaller. The materials from which the rods are fabricated should have very high dimensional stability. Ceramic rods appear to possess this stability but it needs to be determined whether they are sufficiently strong to survive the vibrations of take-off and landing. The design of the quadrupole will be influenced by its dimensions. The equations which describe the operation of the quadrupole indicate that high resolution at low power is best obtained with a structure which is long in the axial dimension. Information is needed on the difficulties encountered in dimensional stability as the length of the assembly is increased.

4. The Ion Detector System

In order to receive all of the transmitted ions the area of the ion collector electrode should be at least as large as the square which could be inserted into the space between the four rods. Unless an unusual geometry is used, this collector electrode is visible from the entrance to the quadrupole analyzer. This means that the collector cannot

be shielded from photons which pass through the entrance aperture. It is impossible to choose materials whose work functions preclude the possibility of secondary emission of electrons by the impingement of photons onto the collector surface. Therefore a system of electrodes and potentials must be designed which will effectively suppress the flow of any current to or from the ion collector as a result of the action of energetic photons which release electrons from surfaces in the vicinity of the collector.

It might seem that the requirements of the ultimate in sensitivity for the system would encourage the use of a secondary emission multiplier to observe the transmission of ions through the mass filter. However, the additional problems which accrue from the use of a secondary electron emission multiplier may outweigh the advantages of its use.

One of the main advantages of the use of a secondary emission multiplier is that of high speed of response. Very little, if any, increase in sensitivity is given through the use of a secondary emission multiplier. Electrometer amplifiers are capable of responding to currents of 10^{-17} amperes. This represents a current flow of only 60 charges per second. In order to minimize the uncertainty owing to the statistical fluctuations of the random ion currents, (ion current shot noise) the mass scanning must be done at a very slow rate if currents of this order are to be observed. This condition is not relieved through the use of a secondary emission multiplier. Thus, it is seen that the secondary emission

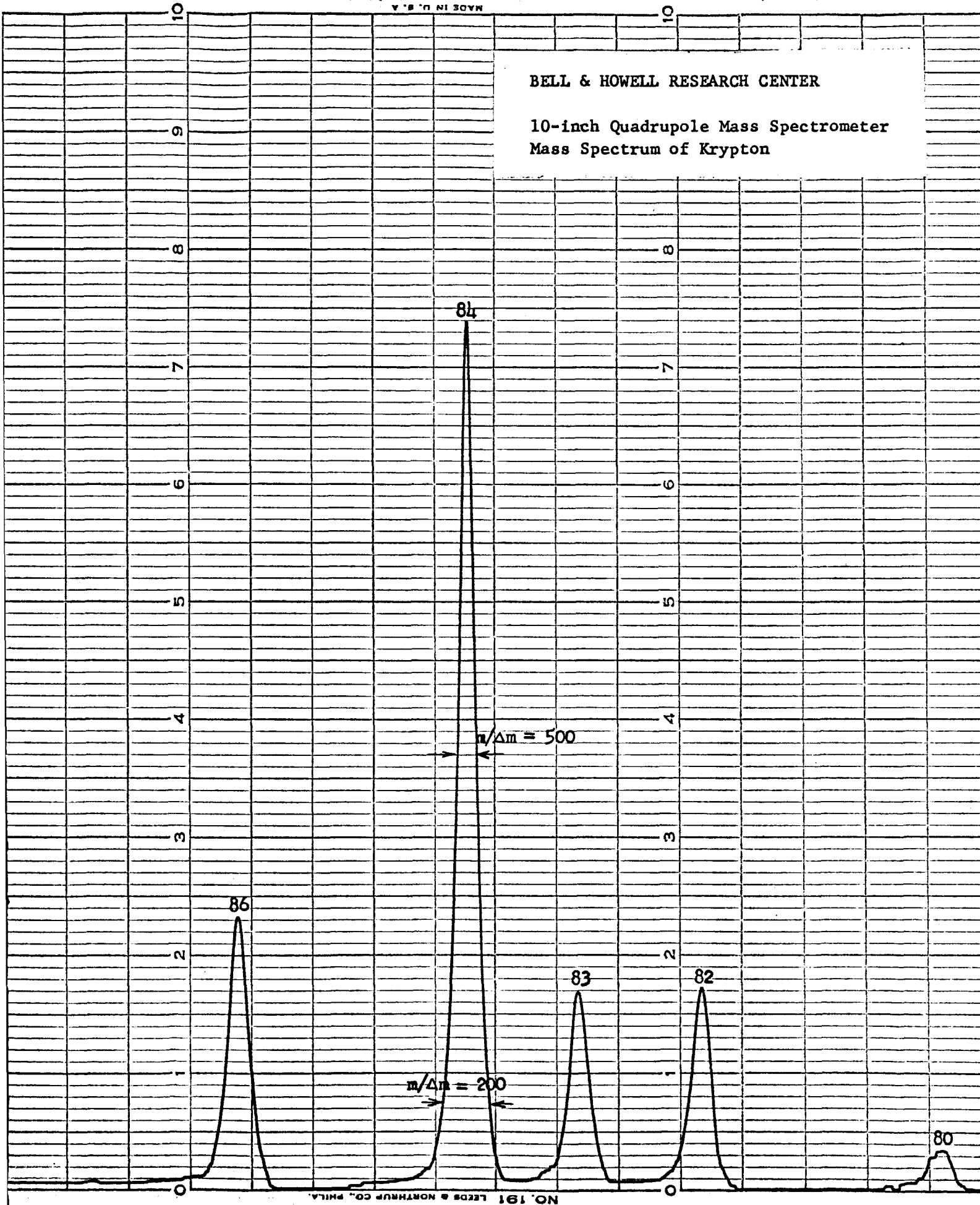
multiplier gives very little if any increase in instrument sensitivity or in the permissible scan speed.

Because of the high voltages and the many surfaces which are present when a secondary emission multiplier is used the problems of rendering the detector system insensitive to the action of the ever-present photons is greatly increased.

Through the use of an unusual geometry, the ion collector electrode can be removed from the line of sight position as seen from the entrance aperture. We have developed in principle a method in which the analyzing quadrupole is followed by a similar quadratic structure in which the electrodes are bent in an arc of the large circle. If this structure is excited with ac voltages only, it becomes a strong focusing structure which will very easily conduct the transmitted ions around the arc of a circle. If this is done, the collector electrode can be placed out of sight from the direct bombardment of the incident photons which pass through the entrance aperture.

In the design of the optimum equipment to be used on the moon, due consideration must be given to the geometry and the potentials of the ion detector system.

BELL & HOWELL RESEARCH CENTER

10-inch Quadrupole Mass Spectrometer
Mass Spectrum of Krypton

Influence of Space Charge on the Potential Distribution in Mass Spectrometer Ion Sources

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The role of space charge as a factor influencing the potentials and potential gradients in a mass spectrometer ion source of the electron bombardment type is calculated. Planar equipotential surfaces are assumed, and the analysis then becomes that of a plane parallel positive ion diode. The "cathode" of the ion diode may be either emission-limited or space-charged-limited. The analysis considers the charge of the electrons in the ionizing sheet and the charge of the positive ions in the diode.

At a critical gas pressure the influences of the positive and negative charges on the potential of the ionizing region are equal and opposite, for small ionizing current. This concept leads to a pressure normalization in terms of the critical pressure. For a given source geometry and electron bombarding energy one can construct universal curves which give the potentials and the potential gradients as a function of the normalized gas pressure and the ratio of the ionizing electron current density to the repeller voltage. Experimental data are in agreement with the predictions of the theory.

INTRODUCTION

AN appreciation of the phenomena which occur in a mass spectrometer ion source of the electron bombardment type is obtained from an analysis of what happens to the potentials and the potential gradients in the source when space charge effects are present. In spite of the small dimensions of such ion sources and the minuteness of the electron and ion currents used, space charges grossly alter the potential (and gradient) distribution. Thus the early portions of the ion trajectories may be sensitively influenced by space charge.

In this work the potential and the potential gradient at the ionizing region are calculated, and the results are presented as a set of general curves using normalized variables. The analytical expressions indicate the influence of ionizing electron current, gas pressure and ionizing probability, and the ion repeller voltage for any combination of these independent variables. The explicit dependence of space charge phenomena on the design parameters of the source geometry is obtained.

For purposes of analysis the equipotential surfaces in the source are assumed to be parallel planes, and any influence of the ion accelerating gradient which "leaks" through the first slit is ignored. Where possible the variables are normalized so that the analysis is carried out in dimensionless numbers.

The knowledge of the actual potential of the ionizing regions, as given in this paper, is of particular importance to one who does appearance potential studies.

GENERAL

The geometry of an idealized mass spectrometer ion source in which the equipotentials are assumed to be portions of parallel infinite planes is given in Fig. 1. The ionizing electron current is shown to flow in a sheet from the filament to the anode in the ionizing plane. Because the anode to which the electrons flow is of relatively small dimensions, it is shown as intercepting only a portion of the current in the large sheet.

The region between the ionizing plane and the first slit plane contains only positive ions, and constitutes a positive ion diode. The "cathode" of this diode is the ionizing plane, and the "anode" is the first slit plane. The gradient on the first slit side of the ionizing plane is frequently not zero, and in these instances the flow of current in the ion diode is emission-limited. The relation between the cathode gradient of an emission-limited plane-parallel diode and the current density is given in the literature.^{1,2} The nomenclature and the results of reference 2 are used throughout this paper.

Typical potential distributions as functions of position between the repeller and the first slit plane are given in Fig. 2. In the absence of any space charge the voltage gradient in the source is uniform, and the potential distribution is given by curve 1. If an ionizing electron current I_1 is added at zero pressure (no positive ions) the electron space charge depresses the potentials as in curve 2. As we hold the ionizing current density constant and admit gas to the source in two consecutive steps the potentials rise as shown by curves 3 and 4. These potential distributions are based on the assumption that no negative ions are formed in the source.

In the course of this analysis it was discovered that it is extremely convenient to normalize the pressure in

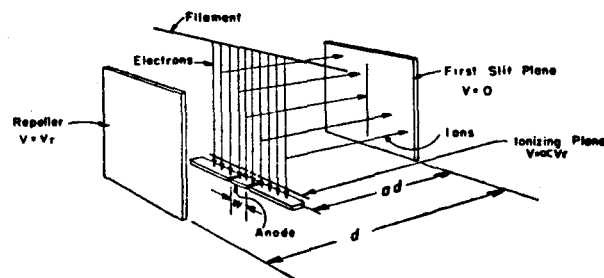


FIG. 1. Geometry of idealized ion source. The electron beam is constrained to the sheet by a magnetic field.

¹ H. F. Ivey, *Phys. Rev.* **76**, 554 (1949).

² W. M. Brubaker, *Phys. Rev.* **83**, 268 (1951).

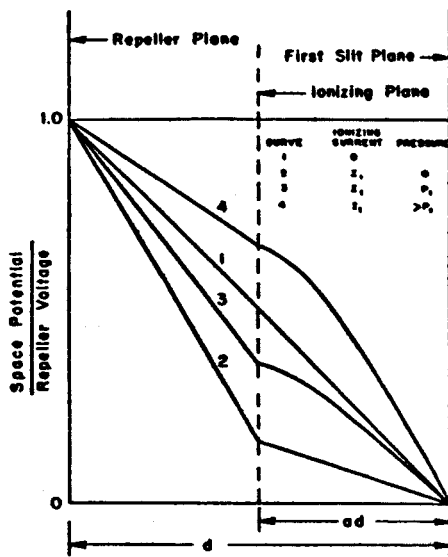


FIG. 2. Space potential vs position for typical conditions of operation. I_1 is an arbitrary value of ionizing electron current which is the same for curves 2, 3, and 4.

the source to that pressure at which, for the ionizing plane, the influence of the electron space charge in the ionizing sheet is exactly neutralized by the positive ion space charge at low ionizing currents. This pressure is noted as P_c , the critical pressure. A typical potential distribution at the critical pressure is shown in Fig. 3.

One of the main objectives is the calculation of the potential of the ionizing region as a function of the geometry, the ionizing current density, the pressure and the ionizing probability of the gas present in the source. This potential is normalized to the repeller potential by the dimensionless variable α . When α is known, several other parameters such as the gradient at the ionizing sheet, the ion current density relative to the space-charge-limited ion current density for the same diode potentials, etc., are also known. The potential of any plane in the source can be calculated with the equations given in reference 2, if desired.

The analysis is divided logically into three regions of increasing ion currents which are assumed to be proportional to the product of the anode current and the pressure. The regions are characterized as follows.

Region I

This region is bounded on the lower end by zero space charge, and on the upper end by the condition of space-charge-saturation (zero gradient) at the cathode of the positive ion diode. The single positive ion diode is emission-limited in this region.

Region II

Zero gradient on the first slit side of the cathode of the positive ion diode and a finite gradient on the repeller side define this region. Thus we have a single space-charge-limited diode.

Region III

At still higher ion currents the ions are formed at such a fast rate that they are not all drawn to the plane of the first slit. This happens when the potential of the ionizing sheet is equal to or greater than the repeller voltage. Thus the positive ion space charge causes the potential of the ionizing region to rise above that of the repeller, and we have zero gradient on both sides of the electron beam, or two space-charge-limited diodes in parallel.

The analysis of region I is made in two parts: one of a low current level, and one of a high current level. From the consideration of the low current level phenomena comes the concept of a "critical" pressure. This proves to be a most useful normalization which greatly aids the analysis at the high current levels.

The definitions of the symbols used are given in Table I. The variable i_v , the anode current in microamperes divided by the repeller voltage, is the only variable whose physical meaning is not obvious. It has the appearance of a transconductance, but the anode current and the repeller voltage are independent of each other. Their influence on the potentials in the source, however, is determined uniquely by their *ratio* independently of their individual magnitudes. This comes about because the influence of the electron beam is to depress the space potentials while the repeller voltage raises them.

In combination with the definitions of Table I, and the concept that the anode intercepts a portion of the electron current which flows in a sheet, i_v is expressed as:

$$i_v = \frac{w_{e1} \times 10^6}{V_r}, \quad (1)$$

$$i_v = \frac{w\sigma \times 10^6}{V_r} \left(\frac{2V_{e1}e}{m_e} \right)^{\frac{1}{2}}. \quad (2)$$

Any dependence of V_{e1} on the potential of the ionizing region is neglected. A form of Poisson's equation in rationalized mks units states

$$\Delta(dV/ds) = \sigma/\epsilon_0, \quad (3)$$

where in our case $\Delta(dV/ds)$ is the difference in the gradient on the two sides of the ionizing plane, and σ is the electron charge per square meter in the ionizing sheet.

The gradient on the first slit side of the ionizing plane is the cathode gradient of the positive ion diode. For emission-limited conditions the normalized density of ion current is related to the normalized cathode gradient by²

$$\rho = \frac{1}{2} + \left(\frac{1}{2} - \frac{3}{4}\gamma \right) (1 + 3\gamma)^{\frac{1}{2}}. \quad (4)$$

Combination of Eqs. (2) and (3) with the definition of

γ leads to

$$i_v = \frac{1}{A} \left[(1-\alpha) - \frac{1-\alpha}{a} \alpha \gamma \right], \quad (5)$$

where

$$A = \frac{(1-\alpha)d \times 10^{-8}}{\epsilon_0 w} \left(\frac{m_e}{2V_{e1}} \right)^{\frac{1}{2}}$$

and is a constant for a given source operated at constant electron energy.

The flow of positive ions through the diode, according to the Child-Langmuir equation and the definition of ρ yields

$$j_{+ion} = \frac{4\rho}{9} \left(\frac{2e}{M} \right)^{\frac{1}{2}} \frac{(\alpha V_r)^{\frac{1}{2}} \epsilon_0}{(ad)^2}. \quad (6)$$

The physics of the ionization process gives us a relation between j_{+ion} and j_{e1}

$$j_{+ion} = \frac{SP_{mm} V_r i_v}{w} \times 10^{-8}. \quad (7)$$

The Eqs. (4) through (7) give us sufficient information to allow us to eliminate any three of the four variables α , γ , ρ , and j_{+ion} , and to express the remaining one as a function of i_v and the source parameters a , d , w , and V_{e1} as given by A .

In region II the diode is space-charge-limited and so ρ and γ have the constant values of unity and zero, respectively. This greatly simplifies the equations.

Analysis, Region I

Low current solution.—The first instance in which approximation for ease of manipulation can be made without loss of accuracy at low levels is in Eq. (4).

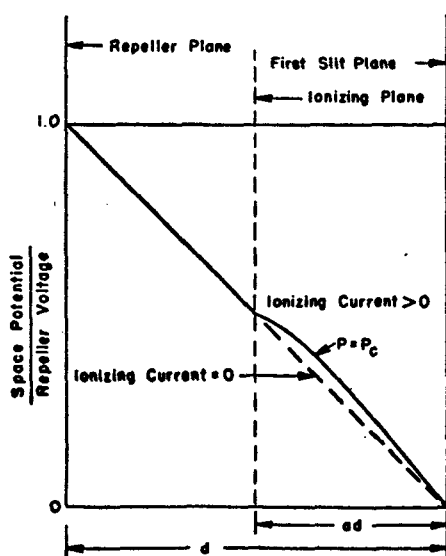


FIG. 3. Space potential vs position when P is the critical pressure, P_c . ($x=1$.)

TABLE I.

V_r	= repeller voltage, volts, relative to the potential of the first slit plane, which is at $V=0$;
αV_r	= potential of the ionizing plane;
V_{e1}	= energy of ionizing electrons, electron volts;
d	= depth of ion source, repeller to first slit, meters;
ad	= distance from ionizing region to the first slit, meters;
e	= electronic charge, 1.6×10^{-19} coulombs;
j_{e1}	= electron current per meter in ionizing sheet;
M	= mass of positive ion, kilograms;
m_e	= mass of electron, 9×10^{-31} kilograms;
j_{+ion}	= ion current density, amperes/sq meter;
i_v	= $\frac{\text{anode current in microamperes}}{\text{repeller voltage, volts}}$;
γ	= $\frac{\text{gradient at the cathode of the positive ion diode in the presence of positive ion space charge}}{\text{gradient at the cathode of the positive ion diode in the absence of positive ion space charge, at the same } \alpha}$;
ρ	= $\frac{\text{actual positive ion current density}}{\text{space-charge-limited positive ion current density, at the same } \alpha}$;
ϵ_0	= permittivity of free space, 8.85×10^{-12} farads/meter;
S	= number of ion pairs formed per electron per meter of electron path at 1 mm Hg pressure;
x	= $\frac{\text{pressure, mm Hg}}{P_c, \text{ the critical pressure, mm Hg}} = \frac{P_{mm}}{P_c}$;
w	= width of ionizing electron sheet intercepted by the anode, meters.

For ρ small (4) becomes

$$\gamma \doteq 1 - \frac{16}{27} \rho. \quad (4a)$$

If we use Eqs. (4a), (5), (6), and (7) to eliminate ρ , j_{+ion} and γ from Eq. (5), we obtain

$$\alpha^{\frac{1}{2}} + \alpha \alpha^{\frac{1}{2}} [A i_v - 1] = \frac{4}{3} a^2 d S P_{mm} \left(\frac{M V_{e1}}{m_e V_r} \right)^{\frac{1}{2}} A i_v. \quad (8)$$

Equation (8) is readily solved for the conditions of small i_v by letting

$$\alpha = a(1 + 2\delta). \quad (9)$$

When Eq. (9) is set into Eq. (8).

$$\delta \doteq \frac{A}{2} \left[\frac{4}{3} d S P_{mm} \left(\frac{a V_{e1} M}{V_r m_e} \right)^{\frac{1}{2}} - 1 \right] i_v. \quad (10)$$

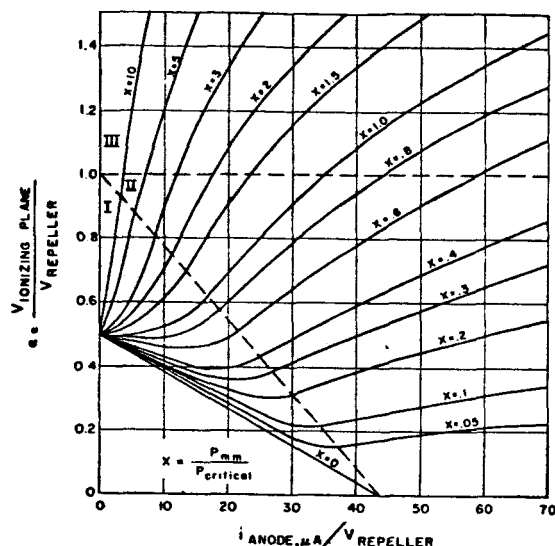


FIG. 4. Potential of the ionizing region as a function of i_v . regions I, II, and III are separated by the two dotted straight lines. The regions are characterized as: region I—one emission-limited diode; region II—one space-charge-limited diode; and region III—two space-charge-limited diodes in parallel.

Equation (10) is entirely satisfactory for the rate of change of δ (or α) with respect to i_v as $i_v \rightarrow 0$. It also shows the possibility of having the potential of the ionizing region independent of i_v . The pressure at which this occurs we shall call the critical pressure, P_c . It is given by

$$P_c = 3(V_m m_e / a V_{01} M)^{1/2} / 4dS, \quad (11)$$

and if we define x by the equation

$$P_m = x P_c \quad (12)$$

Eq. (10) becomes

$$\delta \doteq (x-1) A i_v / 2 \quad (13)$$

and Eq. (9) becomes

$$\alpha \doteq a[1 + A(x-1)i_v]. \quad (14)$$

For i_v small this is an excellent approximation.

The approximate solution as represented in Eqs. (13) and (14) is sufficiently accurate for many of the operating conditions found in actual practice. However, it is not applicable in all cases, and so it is expedient to consider the phenomenon without the approximations.

Large current solution.—If we combine Eq. (11) for the critical pressure with the Eqs. (4) through (7) we can calculate the potential variations and display the results for any given source in a set of curves in normalized variables. A combination of Eqs. (5), (6), (7), (11), and (12) yields

$$\frac{1-a}{1+\frac{a}{\rho}} = \frac{4}{9a} \left[\frac{2(1-a)}{A} \right]^{\frac{1}{2}} (i_v^{-1} - A i_v)^{\frac{1}{2}} \quad (15)$$

or

$$F(\gamma, \rho) = x^{-1} G(i_v). \quad (16)$$

The explicit form of Eq. (16) is too complicated for direct computation. However, $F(\gamma, \rho)$ can be plotted as a function of either γ or ρ for a given source. Similarly, $G(i_v)$ can be plotted as a function of i_v . Then, using x as a parameter, families of curves can be obtained relating γ and ρ to i_v . Further, α as a function of i_v can be obtained from γ through the use of Eq. (5).

Analysis, Region II

In region II the positive ion current flows across the diode under space-charge-limited conditions at the ionizing sheet. The relation between the ion current density and the voltage across the diode is given by the Child-Langmuir equation

$$j_{+ion} = \frac{4}{9} \left(\frac{2e}{M} \right)^{\frac{1}{2}} \frac{(\alpha V_r)^{\frac{3}{2}}}{(ad)^2} \epsilon_0.$$

As the rate of ion production is uniquely determined by the anode current (of ionizing electrons), the ionizing probability, and the pressure of the gas in the source, it is the independent variable and the voltage the dependent variable. Thus, we can state

$$\alpha_{\text{region II}} = \alpha_{\text{boundary regions I and II}}$$

$$\times \left(\frac{i_{v \text{ region II}}}{i_{v \text{ boundary regions I and II}}} \right)^{\frac{2}{3}}. \quad (17)$$

Analysis, Region III

In region III α is greater than unity. Thus, ions flow in both directions from the ionizing region as space-charge-limited current. Again, the rate of production of the ions is assumed to be entirely independent of the potential of the ionizing region. The potential of the region adjusts itself so that the sum of the two diode currents is equal to the rate of ion production.

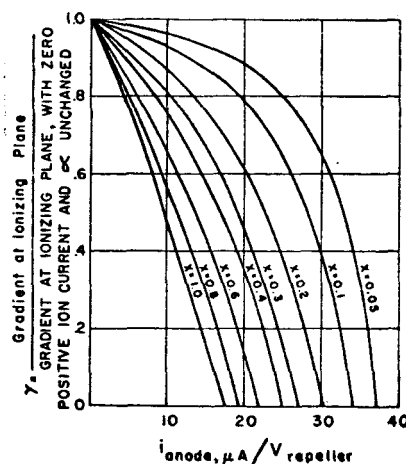


FIG. 5. Potential gradient at the ionizing plane as a function of i_v . The normalization is to the positive ion diode variables.

If we denote the ion current density to the first slit plane as j_1 , and that to the repeller as j_2 , we have

$$j_1 = \frac{4}{9} \left(\frac{2e}{M} \right)^{\frac{1}{2}} (\alpha V_r)^{\frac{1}{2}} \epsilon_0 / (ad)^2 \quad (18)$$

$$j_2 = \frac{4}{9} \left(\frac{2e}{M} \right)^{\frac{1}{2}} [(\alpha-1)V_r]^{\frac{1}{2}} \epsilon_0 / [(1-a)d]^2 \quad (19)$$

and

$$j_1 + j_2 = SP_{mm} j_{el} = \frac{4 \left(\frac{2e}{M} \right)^{\frac{1}{2}} V_r^{\frac{1}{2}} \epsilon_0}{9d^2} \left[\frac{\alpha^{\frac{1}{2}}}{a^2} + \frac{(\alpha-1)^{\frac{1}{2}}}{(1-a)^2} \right] \quad (20)$$

If we normalize the pressure as by Eqs. (11) and (12) this becomes

$$i_v = \frac{16\epsilon_0 w \times 10^6}{27\pi d} \left(\frac{2aeV_{el}}{m_e} \right)^{\frac{1}{2}} \left[\frac{\alpha^{\frac{1}{2}}}{a^2} + \frac{(\alpha-1)^{\frac{1}{2}}}{(1-a)^2} \right] \quad (21)$$

$$= B[\alpha^{\frac{1}{2}} + C(\alpha-1)^{\frac{1}{2}}] / x \quad (22)$$

where B and C are constants for a given source operated at constant electron ionizing energy.

APPLICATION OF THE THEORY

A set of universal curves has been made for a typical ion source of the electron bombardment type. The data for the source are given as follows: $a=0.5$, $d=0.1$ inch $= 2.54 \times 10^{-2}$ meter, $w=0.05$ inch $= 1.2 \times 10^{-2}$ meter, and $V_{el}=70$ volts.

The dependence of the potential of the ionizing plane upon i_v is shown in Fig. 4. The three regions are separated by the dotted straight lines. It is interesting to note that at low pressures the boundary between regions I and II is reached essentially as a result

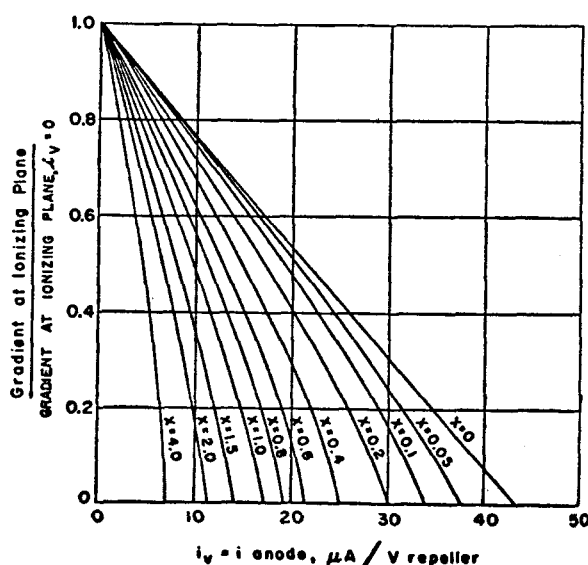


FIG. 6. Potential gradient at the ionizing plane as a function of i_v , normalized to the gradient when $i_v=0$.

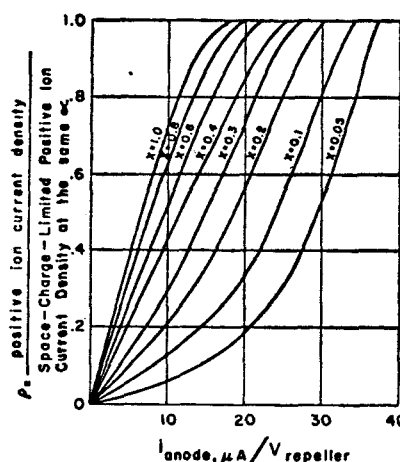


FIG. 7. Space-charge-saturation of positive ion current as a function of i_v , normalized to positive ion diode variables.

of the space charge of the electrons which lowers the potential across the positive ion diode to very low levels. At pressures above $x=1$ the potential of the ionizing region always increases with i_v , and at the higher pressures the potential of the ionizing region rises quite rapidly with i_v .

The normalized gradient on the first slit side of the ionizing region is shown in Fig. 5. γ is defined in terms of the positive ion diode variables. Thus the gradient to which the data of Fig. 5 are normalized is the gradient which would exist if the potential of the ionizing region remained constant while the pressure was reduced to zero.

Because the normalization of γ is to a gradient which is not experimentally realizable, it is interesting to plot the actual gradient normalized to its value at $i_v=0$. To do this we multiply by α/a . This is done in Fig. 6. Here we see the influence of space charge on the gradient at the ionizing plane. It is obvious that this gradient is decreased by both the electron and the ionic space charges.

The normalized positive ion current density, ρ , as a function of i_v , is given in Fig. 7. Here again we see that at low pressures space-charge-limited conditions are reached primarily because the electron space charge lowers the diode voltage. At the higher pressures the rate of approach to space-charge-limited conditions is slowed by an increase of the diode voltage caused by the positive ion space charge. The normalization is in terms of the diode variables.

EVALUATION OF THE APPROXIMATIONS

In order to facilitate a mathematical statement of the problem, two simplifying assumptions were made: (A) All equipotentials are parallel planes; and (B) the ionizing sheet of electrons is of infinitesimal thickness.

Neither of these is realized in practice. Assumption (A) makes the greater departure from reality, as the dimension of the electron beam in the direction parallel

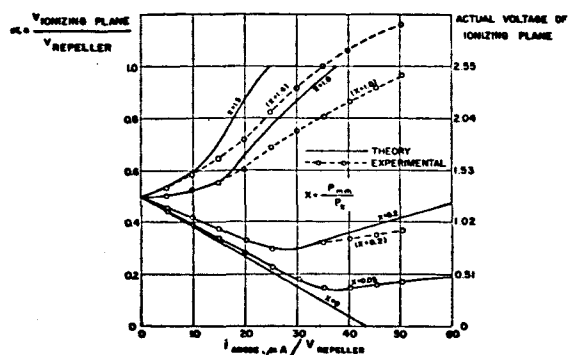


FIG. 8. Comparison of theory and experiment. The anode current was empirically adjusted to fit the low pressure curve, $\alpha=0.05$. Remaining data were then plotted without further adjustment.

to the repeller plane is quite small. This causes the capacity of the ionizing region to be much greater than it otherwise would be. In addition the warping of the equipotentials in the vicinity of the space charge may be expected to have an important influence on the optical properties of the source. This may well be the mechanism of the influence of the presence of a second gas on the sensitivity of the instrument to a first gas.

Assumption (B) is of lesser importance. The influence of space charge on potentials outside the volume in which the charges reside is essentially a function of the total charge involved and independent of the distribution of the charges. Thus outside the ionizing region itself the potentials are relatively unaffected by the thickness of the electron beam. This paper ignores the distribution of potentials and gradients within the ionizing sheet, but it is felt that the conclusions drawn are little influenced by the distribution of electron current in the direction perpendicular to the plane of ionization.

EXPERIMENTAL VERIFICATION OF THE THEORY

The soundness of the analysis is supported by experimental data which relates the potential of the ionizing region with anode current, repeller voltage, and the pressure. The data shown in Fig. 8 were taken by observing the change in ion accelerating voltage required to keep the ion beam on the collector of the mass

spectrometer as the anode current and the pressure were varied. The actual potentials of the ionizing region are given as well as the relative values in terms of α .

The anode current as plotted was normalized to fit the theoretical curve at the lowest pressure, and then the rest of the data were taken without further normalization. This empirical normalization is required because the electron beam is not in the form of a very broad (infinite) sheet, as was assumed for purposes of calculation. The capacity per unit area of the ionizing sheet is greater because of its finite size.

Since the influence of the electron space charge on the potential of the ionizing region varies inversely as the electrostatic capacity of the beam to its environs, we would expect the dependence of the space potential on the electron beam to be less than that calculated for infinite sheets. The same argument applies to the ions. In Fig. 8 the actual anode currents have been reduced by an arbitrary factor of 1.65 to obtain the degree of agreement shown between experiment and theory.

CONCLUSIONS

The essential characteristics of the potentials and gradients in a mass spectrometer ion source are derived by treating the ion accelerating region as an emission-limited or space-charge-limited diode as the conditions require. A comparison of the theory with experimental data shows that the theory is correct in its essentials. When allowance is made for the increased capacity of the ionizing region owing to its finite size, the agreement between experiment and theory is satisfactory.

The knowledge of the dependence of the source potentials on the source variables (ionizing current, repeller voltage, pressure, etc.) is vital for appearance potential investigations. It is also necessary for an understanding of the influence of space charge on the optical properties of the source.

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